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PROPERTIES OF REACTIVE ATOMIC

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AND THEIR LOW TEMPERATURE REACTIONS

TO FORM NOVEL SUBSTANCES

June 1, 1978 to August 31, 1979

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Department of Chemistry

The Pennsylvania State University



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Scientific Personnel who have worked on and received income from this program:

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Jerry Dobson
John Kennan
Donald May
Chris Moon
Shelley Niznik
Robert Remick
Alan Shobert
Robert Tlumak
Bruce Wilburn

Until 1975 support came exclusively from AFOSR. For the succeeding triennium, with contracting funds, the same level of support was maintained with support from two sources, AFOSR ~65%, NSF ~35%.

During the early parts of the current triennium the graduate student involvement in this program fell dramatically; the causes were forced on us. Since then there has been a substantial recovery, but without the recovery of the free grant fellowships (no longer exist), which made very important contributions in earlier years. For the main, funds were expended in support of foreign nationals from whom the immediate return was small, but the long term effect from this period learning atom methods will be large. In each instance a cooperative program has been, or will be established and joint publications will be the end result, with no further dependence on our funds. These circumstances caused a temporary sharp decrease in completed work suitable for publication, a condition which is now overcome with the enthusiastic return of American students. During this period training of individuals was an important component, and the application of the limited manpower to extending the scope of this field was deemed more important than working intensively within the narrow scope required to produce the finishing touches. We have a number of subjects ~~which~~ are ready for write-up, or are already in manuscript form; it is estimated that between fifteen and twenty publications will be sent to the journals during the next twelve months. The following is a summary of these activities:

Atom EMF Series — Electron transfer properties of atoms are correlated with a new ~~Electron Series~~ EMF series called the atom EMF series; they do not correlate with standard potential values since the latter are determined by the free

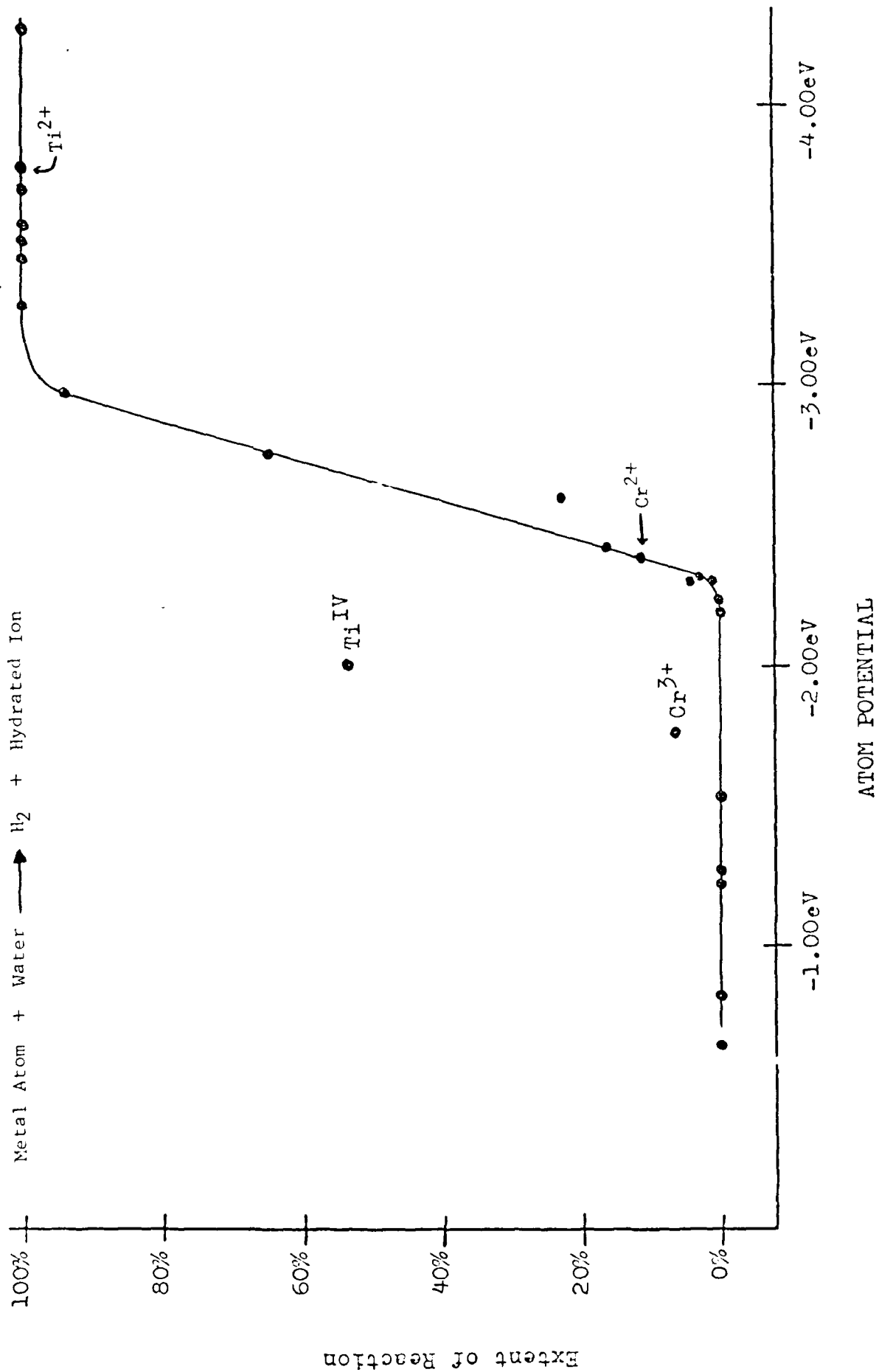
energy change for metal converting to hydrated ion. To correlate atom properties a free energy change is required for the conversion of atom to hydrated ion. A good approximation of this latter value is obtained by adding to the standard potential the free energy of vaporization. This atom EMF series correlates nicely with the electron transfer properties studied so far (vide infra). The limitation in developing the full atom EMF series is the lack of information on hydration energies of the ions. Nonetheless this is a very useful concept for correlating electron transfer properties of atoms, and since all atoms can be placed in sequence in the atom EMF series (see water reactions, below), it now becomes possible, with a Born-Haber cycle, to arrive at an approximation for the unknown ion hydration energies.

An interesting feature is the result that copper and zinc have nearly identical atom potentials and atom reactivities; the large difference in standard potentials (and reactivity for the metals) is now attributed to the large differences in heats of vaporization. It is gratifying to find these atomic neighbors have similar properties, and also to have an explanation for the large differences in the reactivities of the metals.

4. Reaction of Metal Atoms with Water: The reactions of the metal atoms with water is being studied in depth (the literature has no information about this reaction). Reactive metals liberate H_2 from water during the co-deposition process, less reactive metals react during warm-up, still less reactive ones do not react.

Reduction Potentials for Bulk Metals and Metal Atoms

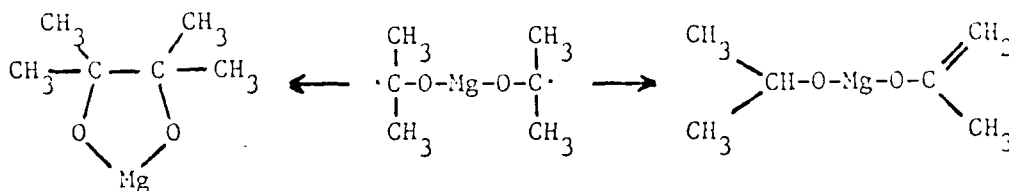
<u>Metal</u>	<u>Ox.State</u>	<u>E°_{metal}</u>	<u>E°_{atom}</u>
Li	1+	-3.07	-4.29
Ti	2+	-1.63	-3.82
Ca	2+	-2.87	-3.69
Y	3+	-2.37	-3.69
V	2+	-1.2	-3.6
K	1+	-2.93	-3.56
Na	1+	-2.71	-3.52
Sr	2+	-2.89	-3.46
Th	4+	-1.90	-3.3
Mg	2+	-2.37	-2.97
Zr	4+	-1.53	-2.77
Ti	2+	-1.12	-2.67
Al	3+	-1.66	-2.60
V	3+	-0.88	-2.46
Mn	2+	-1.17	-2.43
Cr	2+	-0.86	-2.37
Co	2+	-0.29	-2.33
Fe	2+	-0.44	-2.30
Mo	3+	-0.2	-2.3
Ni	2+	-0.25	-2.22
W	IV	-0.12	-2.2
Ti	IV	-0.88	-1.97
Cr	3+	-0.73	-1.75
Sn	2+	-0.14	-1.53
Zn	2+	-0.76	-1.25
Cu	2+	+0.34	-1.22
Fe	3+	+0.33	-0.91
Cd	2+	-0.40	-0.81
Rh	2+	+1.2	-0.63



This property correlates perfectly with the atom potential values. An experimental descending reactivity series is Li, Ca, Y, K, Na, Sr, Th, Mg, Zr, Al, Mn, Fe, Co, Mo, Ni, W, Zn, Cu, Rh, Cd. The mechanism of hydrogen formation has been probed in several ways, and appears to be one in which there is found initially the hydrated ion and the solvated electron.

Low Sticking Coefficients of Metals; The atoms Mg, Zn, Cd, Ca and Y follow non-linear pathways to the walls of a reactor flask, 90-100% of them arriving there even though 30-50% of them must encounter first the mechanical obstructions such as electrodes, inlet systems, etc., on which they are expected to condense. It has been confirmed by simple experiments that these atoms bounce off walls at room temperature despite their low equilibrium vapor pressure which should make their sticking coefficients unity, a value well-established for other metal atoms. This is by no means a new type of observation: L. Knight reported recently on the low sticking coefficient of magnesium on halide treated glass and there are earlier observations on zinc. As a consequence, transport of atomic vapors of these metals around corners is feasible, a property which could prove valuable when light or heat sensitive substrates are employed.

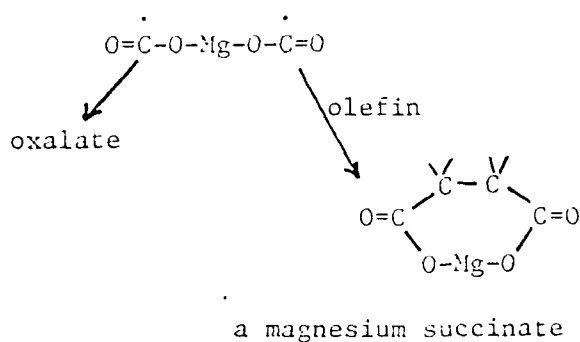
Reactions of Magnesium Atoms with Acetone; The major product is magnesium pinacolate, minor but important are the magnesium enolate of acetone and isopropoxide in 1:1 ratio. The double ketyl is a reasonable intermediate. The deoxygenation of acetone to the carbene (reported by other laboratories)



a bis-ketyl

seems to be a gas phase reaction which becomes more prominent with increasing flux of metal atoms, this process disappearing at low metal atom flux. Our laboratory, Wescott's (Christian Brothers College) and Klabunde's (U.N. Dakota) have made independent entries into this field.

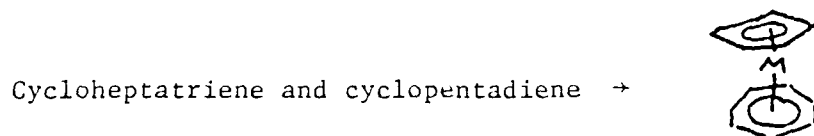
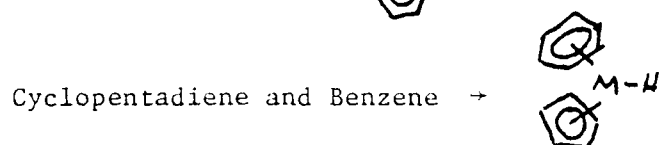
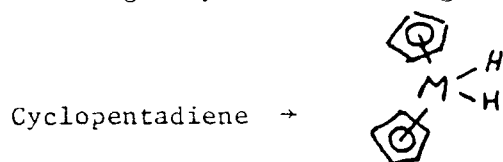
Reactions of Metal Atoms with Carbon Dioxide. Extensive deoxygenation occurs when magnesium or aluminum atoms react with a CO_2 matrix, making some carbon, but mainly oxalate as product. More interesting is the controlled reduction of carbon dioxide by magnesium atoms in the presence of olefins; this leads to addition of a carboxyl on each carbon of the double bond, making succinic acids from olefins. Bis-carboxylations of olefins was an unknown reaction prior to this finding. An intermediate similar to that proposed in pinacol formation may be involved.



Bis-Arene Transition Metal Complexes, Many members of this family are known, prepared by classical methods. The direct condensation of metal atoms with arenes has added significantly to this family of compounds, making available derivatives previously not known, benzenes with substituent halogens, methoxyls, carbethoxyls, dimethylamino groups. Further, bis-arenes of tungsten, molybdenum and titanium were either unknown or had been made in very poor yield. Our vaporization techniques make these compounds readily accessible. By similar

methods we have prepared bis-arenes of zirconium, thorium, iron, cobalt and nickel; each of these provides a new opening wedge into organometallic chemistry of these elements. The bis-arenes of the iron triad are not stable at room temperature, thus necessitating a spectroscopic study to show the close similarity to the more stable bis-arene chromiums. The kinetic competition of molybdenum atoms for arenes shows the formation of the bis-arenes takes place with only small discrimination between variously substituted arenes.

Reactions of Mo and W with Non-Aromatic Carbocycles. The following reactions occurred in good yields on mixing the Mo or W atoms with the hydrocarbons:



Reactions of Bis-Arene Ti, Zr, with Cyclooctatetraenes. This combination makes a convenient alternate route to cyclooctatetraene derivatives. The 18-electron mixed complexes, arene-cyclooctatetraene, are unstable in the presence of excess cyclooctatetraene. Mono and binuclear complexes of titanium have been isolated; the latter, triscyclooctatetraenedititanium was shown to be a paramagnetic substance (2 unpaired electrons). This binuclear complex is readily reduced to its diamagnetic dianion, a first member of this new class of triple decker anions. From bis-toluene zirconium both mononuclear and polynuclear cyclooctatetraene complexes are obtained; the latter are particularly intriguing since they are likely to have a stacked structure.

Reactions of Bis-Arene Fe, Co, Ni. The stabilities of these arene complexes decreases in the order shown, the nickel complex being unstable below -90° in toluene solution, the iron below -30° . At temperatures lower than these decomposition temperatures these are highly versatile reagents for syntheses. The nickel compound was converted readily to $\text{Ni}(\text{PMe}_3)_4$, and to cyclopentadienylcyclopentenylnickel. The cobalt compound reacts with cyclopentadiene to make cyclopentadienylcyclopentadienecobalt and the iron into toluenecyclopentadieneiron which can be isomerized to cyclopentadienylcyclohexadienyliron. Reactions with butadiene are discussed below.

Reactions of Nickel Atoms with Butadiene. Nickel atom reactions are successful for the preparation of the 1,3-butadiene cyclotrimerization catalysts which are currently employed in German industrial production. The competition of methods for preparing this catalyst will be settled purely on the basis of economics; the long term outcome is still in the balance. Further work is directed at an understanding of what other intermediates are involved in this system. We have submitted to Inorganic Synthesis a procedure for making dodecatrienylnickel from nickel atoms and butadiene, by allowing the initially-formed low temperature matrix to warm to -20° at which temperature the trimerization to the C_{12} species occurs rapidly in the presence of excess butadiene. Also, we have found that at -100° a red 1:1 complex of butadiene-nickel can be isolated which contains discrete C_4 units, but detailed structure still not known. If this latter warms to room temperature it converts to a low molecular weight toluene-soluble polymer which still has the same composition, 1:1. Hydrogenation of the red material produces butane, hydrogenation of the polymer produces an alkane of high molecular weight. The unraveling of the structures is in progress.

Identification of Al-Al Bonded Structures. Internal olefins such as 2-butenes react with Al atoms to make a product of 1:1 composition; terminal olefins react in 3:2 ratio. The 1:1 products have a ladder structure held together by Al-Al bonds. Until recently structural units of this kind had been postulated, but in each instance discredited, except for the recent report from Müllheim of an unstable R_4Al_2 with bulky R's. Our compound reacts with D_2O to produce D_2 (no HD and therefore no Al-H), and with I_2 to split the Al-Al bonds without affecting the carbon-aluminum bonds. The evidence for Al-Al bonds seems conclusive.

Monoatomic Rhodium Supported Catalysts. Heterogeneous catalysts consisting of rhodium atoms dispersed on carbon and on zeolite have been prepared. According to the experts there is no physical method for recognizing this structural feature, only chemical methods. For example, hydrogenation of olefins is known as a structure insensitive reaction: specific rates do not depend on the degree of dispersion. We have shown that the relative reactivities of a set of olefins is changed by annealing of our monoatom-dispersed catalysts at $200^\circ C$. The annealed catalyst must have metal domains, the un-annealed catalyst must have structurally different active sites. The rational synthesis used for this preparation makes the monoatom-disperse structure highly probable. All phases of the preparation and activation are carried out at low temperatures ($-20^\circ C$) to avoid the growth of metal domains which occur at higher temperatures. These catalysts are very reactive, very rapid gas phase hydrogenation of olefins occurring at -20° . Also the catalysts seem to have excellent stability. These successful preparations hold the promise of rational syntheses of supported catalysts whose active sites could be selected to be exclusively monoatom, homo- or hetero -diatom or -triatom sites. This could be a major contribution to the rational synthesis of "molecular metal" supported catalysts. The active sites would differ from those in polymer-supported catalysts, which are being

prepared in many laboratories, in that the atoms are individually bound on a surface without the presence of surrounding ligands.

Metathesis Polymerization; Norbornene and norbornadiene undergo rapid metathesis-type polymerization at -20° in the presence of catalytic amounts of molybdenum or tungsten atoms. Although these atoms do not catalyze the metatheses of simple olefins, clearly they must be the simplest type of catalyst for this family of reactions. Work in this area is the basis for an anticipated Exchange Program in Catalysis with the USSR, specifically with Academician Dolgoplosk (Moscow); this is currently under consideration.

Structures of Tris-butadiene Molybdenum and Tungsten, These eighteen electron compounds have not been synthesized by any method other than our atom based preparation. They are stable yellow materials, and they were the subject of a satisfactory x-ray structure determination. They have an unusual coordination pattern, trigonal prismatic, with planar cisoid butadiene moieties having long C_2-C_3 bonds ($1.55^{+0.08}$ Å).

Infrared Studies. Extensive co-operative work (Prof. Hisatsune) has been carried out, studying low temperature matrix IR spectra on a variety of systems related to the above problems, much of which is in condition for publication. Publication is held in most cases until full correlation of spectroscopy and reaction chemistry is obtained. Some of the systems for which extensive data exists are Fe, Co, Ni, Mg, Pd, Cr in interactions with mono-enes, di-enes, arenes, alkyl halides. CO_2 , acetone, ethers.

Organocopper Compounds, Reaction of copper atoms with carbon tetrachloride produces a green solid, insoluble in CCl_4 , which decomposes to produce $(CuCl)_n$, C_2Cl_4 and C_2Cl_6 . The green solid reacts with HCl and Br_2 to make $CHCl_3$ and $BrCCl_3$, respectively, and with cyclohexene to make dichloronorcarane. A reasonable formulation is $(Cl-Cu-Cu-CCl_3)_n$ from CCl_4 , $(Cl-Cu-Cu-CF_2Cl)_n$ from

CF_2Cl_2 . Analogous green organocopper compounds are obtained by reaction of copper atoms with aryl halides.

Succinimidyl Radical. The chemistry of succinimidyl radical is extensively understood now. Early this radical was postulated as an intermediate in allylic brominations using N-bromosuccinimide, and then the suggestion was disproven. The chemistry of this radical was essentially unknown prior to our involvement. We know how to prepare the radical and ensure that it is the carrier radical in chain reactions. This radical is an avid H-abstractor of low selectivity, similar to chlorine atoms. Also, it adds readily to olefins and to the arene nucleus giving, respectively, 1,2-adducts (N-substituted β -bromoamines) and N-substituted arenes; these substrates are aminated. A theoretical aspect of some significance is the experimental demonstration that two different succinimidyl radicals are involved in our reactions. These have been identified as π - and σ -radicals. Contrary to "popular belief" these are not canonical structures contributing to a hybrid, but isomeric radicals, a consequence of their orthogonal orbital systems. This is a conclusion with general consequences. All of this work was discussed in a Plenary Lecture at the August 1977 Chicago ACS Meeting.

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Recent Plenary Lectures at International Meetings:

International Conference on Organometallic Chemistry, September 1979, Dijon, France.

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Boston Area Organometallic Colloquium, December 1979, Boston, Massachusetts.